# CHANGES IN THE STRUCTURE OF SISAL AND FLAX LIGNINS DURING SODA-AQ PULPING AND TCF/ECF BLEACHING

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## ABSTRACT

The structural modifications of lignins from sisal and flax during their soda-anthraquinone (AQ) pulping and subsequent totally chlorine-free (TCF) and elementary chlorine-free (ECF) bleaching have been studied. For this purpose, residual lignins were isolated from pulps, analyzed by Py-GC/MS and 2D-NMR, and their characteristics compared to the "milled-wood" lignin of the raw materials. Soda-AQ pulping caused a preferential removal of S-lignin and cleavage of β–*O*–4′ linkages but the structure of the residual lignin remained relatively similar to native lignin. TCF bleaching barely affected the lignin structure, and noticeable amounts of β–*O*–4′ linkages still occurs in these pulps. In contrast, ECF bleaching caused strong modifications in the lignin structure with the complete removal of lignin markers in ECF-bleached sisal pulp. However, residual lignin was still present in ECF-bleached flax pulp, with a predominance of G- and H-lignin units and the presence of β–*O*–4′ linkages.

**Keywords**: flax, sisal, residual lignin, pulping, bleaching

## INTRODUCTION

High-quality paper pulps are obtained by chemical pulping processes that partially depolymerize and dissolve the lignin acting as glue between wood fibers. Due to its recalcitrant nature, a certain amount of lignin remains in pulp and, because of its oxidative alteration during cooking, is responsible for the dark color of chemical pulps. The detailed knowledge of the structure of the residual lignins in pulp will provide useful information of the structural changes produced during soda-AQ pulping as well as during TCF and ECF bleaching. Increasing the knowledge of the chemistry of delignification and bleaching will facilitate the search for technical solutions aiming at increasing pulping and bleaching efficiency. In this work, we studied the chemical modifications of the lignin during soda-AQ pulping of two nonwoody materials, sisal and flax fibers, and their subsequent TCF and ECF bleaching. Sisal and flax fibers were selected because of their very different lignin content and composition [1,2].

## MATERIAL AND METHODS

Sisal and flax fibers and their pulps were supplied by CELESA pulp mill (Spain). The MWLs were obtained according to the classical procedure [3] and the residual lignins by acid hydrolysis according to the procedure already described [4]. Pyrolysis of the isolated residual lignins was performed with a 2020 micro-furnace pyrolyzer connected to an Agilent 6890 GC/MS system equipped with a DB-1701 (Agilent J&W) fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 µm film thickness) and an Agilent 5973 mass selective detector (EI at 70 eV). 2D-NMR spectra of isolated lignins were recorded on a Bruker AVANCE 500 MHz.

## RESULTS AND DISCUSSION

### Py-GC/MS

The composition and relative molar abundances of the compounds released after Py-GC/MS of the residual lignins isolated from sisal and flax pulps, and their respective MWL are shown in the **Table**. The Py-GC/MS data indicate a 1:22:77 (H:G:S) relative composition and a high S/G ratio of 3.5 for sisal MWL. Interestingly, the residual lignin isolated from the unbleached sisal soda-AQ pulp presented a pyrogram similar to that of the MWL, with a high predominance of S-lignin compounds (H:G:S composition being 4:32:64), although their relative abundances clearly decreased with respect to the G-lignin units, resulting in a reduction of the S/G ratio to 2.1. This

fact indicates a preferential removal of the S-lignin moieties in sisal during soda-AQ pulping. Interestingly, the pyrogram of the residual lignin from TCF-bleached sisal pulp was rather similar to that of the unbleached sisal pulp, with a predominance of S-units (H:G:S of 2:28:70), and a high S/G ratio. In contrast, the Py-GC/MS analysis of the supposedly "residual lignin material" isolated from ECF-bleached sisal pulp, indicated the total absence of lignin markers in this sample, which reveals that lignin has been completely removed from sisal pulp during ECF bleaching.

**Table 1- The composition and relative molar abundances of the compounds released after Py-GC/MS of the residual lignins isolated from sisal and flax pulps, and their respective MWL.**

| Compound | sisal pulps | | | | flax pulps | | | |
|---|---|---|---|---|---|---|---|---|
| | MWL | Unbleached | TCF | ECF | MWL | Unbleached | TCF | ECF |
| phenol | 0.4 | 0.7 | 0.3 | - | 2.2 | 2.6 | 2.2 | 8.4 |
| hydroxybenzaldehyde | 0.0 | 0.3 | 0.2 | - | 0.0 | 0.4 | 0.6 | 4.5 |
| 2-methylphenol | 0.2 | 0.4 | 0.4 | - | 1.6 | 2.1 | 1.3 | 4.1 |
| 4-methylphenol | 0.2 | 1.2 | 0.8 | - | 5.1 | 2.9 | 3.2 | 13.6 |
| guaiacol | 3.7 | 5.4 | 4.5 | - | 13.0 | 14.8 | 16.5 | 19.1 |
| C2-phenol | 0.2 | 0.6 | 0.4 | - | 1.9 | 1.8 | 2.4 | 1.3 |
| methoxybenzaldehyde | 0.0 | 0.4 | 0.3 | - | 0.0 | 1.0 | 0.6 | 6.1 |
| methylguaiacol isomer | 0.3 | 0.9 | 0.7 | - | 0.0 | 1.3 | 0.5 | 0.0 |
| 4-methylguaiacol | 3.6 | 7.2 | 7.0 | - | 21.2 | 20.7 | 18.2 | 9.3 |
| 4-ethylguaiacol | 1.6 | 3.6 | 3.9 | - | 5.4 | 6.7 | 7.0 | 3.2 |
| methoxycatechol | 0.0 | 1.5 | 2.9 | - | 0.0 | 0.0 | 0.0 | 0.0 |
| 4-vinylguaiacol | 4.2 | 6.3 | 4.8 | - | 14.7 | 15.4 | 15.2 | 4.5 |
| syringol | 15.1 | 13.8 | 11.9 | - | 3.4 | 2.4 | 3.1 | 0.0 |
| eugenol | 1.0 | 0.8 | 0.9 | - | 1.9 | 1.9 | 1.7 | 2.3 |
| 4-propylguaiacol | 0.1 | 0.0 | 0.0 | - | 0.0 | 0.8 | 0.7 | 0.9 |
| syringol-isomer | 0.0 | 1.1 | 1.9 | - | 0.0 | 0.0 | 0.0 | 0.0 |
| *cis*-isoeugenol | 1.1 | 0.8 | 0.9 | - | 1.4 | 1.9 | 1.5 | 1.1 |
| vanillin | 1.5 | 1.5 | 1.3 | - | 3.1 | 4.2 | 4.6 | 4.4 |
| 4-methylsyringol | 14.2 | 16.0 | 17.1 | - | 3.3 | 2.3 | 1.5 | 0.0 |
| *trans*-isoeugenol | 4.4 | 2.5 | 2.3 | - | 8.7 | 7.0 | 8.1 | 3.1 |
| acetoguaiacone | 0.5 | 1.1 | 0.5 | - | 1.6 | 1.4 | 1.4 | 1.8 |
| vanillic acid methyl ester | 0.0 | 0.0 | 0.0 | - | 0.3 | 0.4 | 0.5 | 0.5 |
| 4-ethylsyringol | 1.6 | 3.6 | 2.9 | - | 0.6 | 0.6 | 0.3 | 0.0 |
| guaiacylacetone | 0.4 | 1.3 | 0.3 | - | 1.9 | 2.4 | 4.5 | 8.7 |
| 4-vinylsyringol | 11.0 | 7.4 | 6.9 | - | 1.8 | 1.9 | 1.3 | 0.0 |
| 4-allylsyringol | 4.5 | 2.6 | 3.1 | - | 0.6 | 0.3 | 0.3 | 0.0 |
| propiovanillone | 0.0 | 0.0 | 0.0 | - | 0.9 | 0.7 | 1.2 | 3.2 |
| 4-propylsyringol | 0.2 | 0.5 | 0.4 | - | 0.1 | 0.0 | 0.0 | 0.0 |
| *cis*-4-propenylsyringol | 3.9 | 2.0 | 2.8 | - | 0.6 | 0.3 | 0.3 | 0.0 |
| syringaldehyde | 6.1 | 3.2 | 4.7 | - | 0.9 | 0.2 | 0.3 | 0.0 |
| *trans*-4-propenylsyringol | 12.4 | 6.6 | 9.1 | - | 2.6 | 0.9 | 0.7 | 0.0 |
| acetosyringone | 1.6 | 2.1 | 2.0 | - | 0.6 | 0.3 | 0.1 | 0.0 |
| syringylacetone | 1.4 | 2.9 | 1.9 | - | 0.5 | 0.2 | 0.1 | 0.0 |
| propiosyringone | 0.7 | 1.1 | 1.0 | - | 0.2 | 0.1 | 0.1 | 0.0 |
| *trans*-sinapaldehyde | 4.0 | 0.7 | 2.2 | - | 0.0 | 0.0 | 0.0 | 0.0 |
| S/G ratio | 3.5 | 2.1 | 2.4 | - | 0.2 | 0.1 | 0.1 | 0.0 |

In the case of flax, the pyrogram of its MWL showed predominantly compounds derived from G-lignin units, with a relative composition of 11:74:15 (H:G:S) and a low S/G ratio of 0.2. The pyrogram of the residual lignin from unbleached flax pulp was similar to that of the MWL and also released predominantly compounds derived from G-lignin units. A slight decrease in the relative abundances of S-units, together with a concomitant increase of the relative abundances of G-units (H:G:S composition being 11:79:10), was observed in the unbleached soda-AQ pulp, thus resulting in a decrease of the S/G ratio to 0.1. This fact indicates that S-lignin units, which are present in low amounts in flax fibers, are preferentially removed during soda-AQ pulping, as also observed in sisal. In the case of bleached flax pulps, the pyrogram of the residual lignin isolated from the TCF-bleached pulp was also similar to that of the unbleached pulp, with a predominance of G-lignin compounds. On the contrary, ECF bleaching strongly modified the structure of the lignin and the pyrogram of the residual lignin isolated from the ECF bleached flax pulp was completely different from that of the unbleached flax pulp. In spite of the low lignin

content in this pulp (kappa number 1), some residual lignin could still be isolated and analyzed. The pyrogram of this residual lignin showed the release of lignin markers and indicated that the lignin has suffered strong structural modifications, with the complete removal of S-lignin moieties and a strong increase in the relative abundances of H-units (H:G:S being 38:62:0). An important increase of the relative abundances of oxidized lignin markers (i.e. guaiacylacetone, propiovanillone) was observed in the pyrogram, indicating that oxidative alteration of the lignin moiety also took place during ECF bleaching.

**2D-NMR**

The HSQC spectrum of sisal MWL (Fig. 1a) confirmed that this lignin is extremely enriched in S-lignin units (S/G 4.0) with high amounts of β–O–4′ linkages (A), and only low amounts of condensed substructures such as phenylcoumarans (β–5′), resinols (β– β′) and spirodienones (β–1′). In addition, the HSQC spectrum indicated that this lignin is highly acetylated at the γ-carbon of the lignin side-chain (A′). The HSQC spectrum of the residual lignin (Fig. 1b) revealed the complete absence of acetylation of the γ-carbon of the lignin side-chain, indicating that acetates have been completely hydrolyzed during soda-AQ pulping. Additionally, a large removal of the β–O–4′ linkages occurred during pulping, although important amounts of these linkages still remained in the residual lignin. The HSQC spectrum also indicated the preferential removal of S-lignin units during cooking.

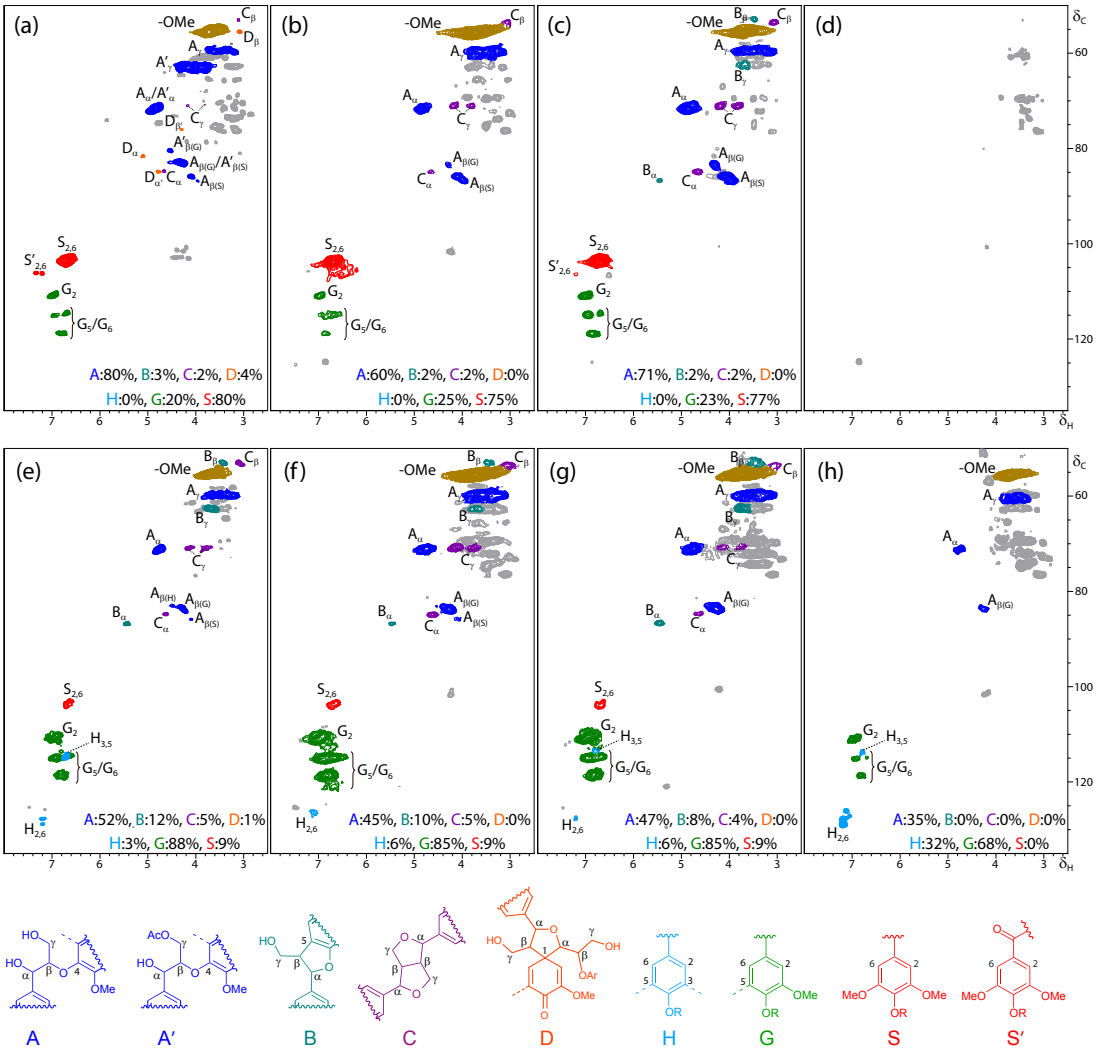


**Fig. 1- 2D-HSQC spectra of the residual lignins isolated from sisal and flax pulps, and their respective MWL. Main structures present in these lignins: (A) β–O–4′ alkyl-aryl ethers; (A′) β–O–4′ alkyl-aryl ethers with acetylated γ–OH; (B) phenylcoumarans; (C) resinols; (D) spirodienones; (H) H units; (G) G units; (S) S units; (S′) Cα oxided S units.**

The HSQC spectrum of the residual lignin from TCF-bleached sisal pulp (Fig. 1c) was also similar to that of the unbleached pulp, with the presence of important amounts of β–O–4′ alkyl-aryl ethers, indicating that TCF bleaching barely affects the structure of the residual lignin. In contrast, 2D-NMR analysis of the supposedly "residual lignin material" isolated from ECF-bleached sisal pulp reveals that lignin has been completely removed from sisal pulp during ECF bleaching (Fig. 1d). The high amounts of S-lignin units and β–O–4′ alkyl-aryl ether linkages in the residual lignin of the unbleached sisal pulp have made this lignin highly susceptible to degradation by chlorine dioxide.

In the case of flax MWL, the HSQC spectrum (Fig. 1e) indicated that it is enriched in G-lignin units. In addition, the main types of linkages present were β–O–4′, followed by β–5′ and lower amounts of β–β′ and β–1′. Comparison with the HSQC spectrum of the residual lignin from unbleached soda-AQ flax pulp (Fig. 1f) indicated a moderate decrease of β–O–4′ during soda-AQ pulping, while the abundance of β–5′ and β–β′ substructures remained largely unchanged. This fact indicates again the preferential removal of β–O–4′ during soda-AQ pulping. As occurs with the residual lignin from unbleached sisal pulp, no oxidized lignin moieties were observed in the HSQC spectrum of the residual lignin from unbleached flax pulp, indicating that depolymerization, instead of oxidation reactions, predominate during pulping. The HSQC spectrum of the residual lignin isolated from the TCF-bleached pulp (Fig. 1g) was also similar to that of the unbleached pulp, with a predominance of G-lignin compounds. In addition, the NMR data indicated that the TCF bleaching barely affects the structure of the residual lignin and the main structural characteristics are maintained. The HSQC spectrum of the residual lignin from the ECF-bleached pulp confirmed the enrichment of H-lignin and the entire removal of S-lignin units after ECF bleaching. However, and surprisingly, the HSQC spectrum clearly indicated that some amounts of the β–O–4′ alkyl-aryl ether linkages still remained in the residual lignin from ECF-bleached flax pulp. Most probably, the enrichment in G- and H-lignin during soda-AQ pulping has made this lignin highly intractable and recalcitrant to chemical degradation.

## CONCLUSIONS

Soda-AQ pulping produced a preferential removal of S-lignin units and β–O–4′ linkages. Despite this, residual lignins were rather similar to native lignin. TCF bleaching hardly affected the lignin structure, and important amounts of β–O–4′ linkages still occurred in the TCF-bleached pulps. ECF bleaching caused strong modifications in the lignin structure, with the complete absence of lignin markers in the ECF-bleached sisal pulp. By contrast, residual lignin could be isolated from the ECF-bleached flax pulp, with a predominance of G- and H-lignin units. Interestingly, β–O–4′ linkages could still be observed indicating the high recalcitrance of flax lignin.

## ACKNOWLEDGMENTS

This study has been funded by the Spanish project AGL2011-25379, the CSIC project 201040E075 and the EU-project LIGNODECO (KBBE-244362). JR thanks the CSIC for a JAE-DOC contract from the program "Junta para la Ampliación de Estudios" co-financed by Fondo Social Europeo (FSE).

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